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characters enumerated in this paper can be employed to good advantage in the identification of species belonging to these genera.

[1] Saccardo, P. A., *Phytophthora cactorum* (C. et L.), *Schroet. Syll. fung.*, 7, 1888, (238).
[2] The complete paper is published in *J. Agric. Res.*, 8, 1917, No. 7.

# A POSSIBLE FUNCTION OF THE IONS IN THE ELECTRIC CONDUCTIVITY OF METALS

By Edwin H. Hall

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Read before the Academy, November 14, 1916

The following paper is a development, in certain particulars, of a suggestion concerning electric conduction in metals which I made in *Il Nuovo Cimento* for January-February, 1915. It rejects the free electrons within the metal as the vehicle of the electric current and puts in their place for this function the metal ions, necessarily equally numerous with the free electrons. Briefly stated, the idea of conduction which I have had in mind is the following:

At very low temperatures the atoms of a metal are packed so closely that electrons pass readily from one to another in a continuous procession through the metal, if there is an applied electromotive force to maintain progression in one direction. Free electrons and metal ions, if indeed ionization exists at the lowest temperatures, need not be called into action here.

With rising temperature the heat vibrations separate the atoms so that they are not always in conductive contact, and not very many degrees above the absolute zero they are, on the average, so far apart that conductive contact between them is exceptional.

In this state of things an electron will not in fact pass from one metal particle to another, even when they are in the closest contact of a collision, unless one of these particles is an atom and the other an ion. Figures 1 and 2 illustrate the fundamental difference, from the point of view of conduction, between an atom-atom collision and an atom-ion collision. In figure 1 the electric force tending to carry the extra electron of the left-hand particle back to the positively charged right-hand particle, just before the particles separate, must be enormously larger[1] than the greatest conteracting force we can apply from without. But in figure 2 the extra electron may belong as much to one particle as to the other, when once the particles meet, and a comparatively small general gradient of potential in the metal, due to an electromotive force applied from without, may well determine what course the electron in question will take.

The experiments and arguments of Professor Bridgman now make it seem probable that I have greatly underestimated the range of temperature through which the normal atoms may, in spite of the heat vibrations, be regarded as remaining in conductive contact with each other, and that, accordingly, the important function which my theory has given to the ions may not belong to them, except perhaps at relatively high temperatures or in the liquid state of the metals.

Nevertheless, the potentiality of the ions for conduction is so great, under certain conditions which do not appear impossible, that it seems worth while to make some exposition of it.

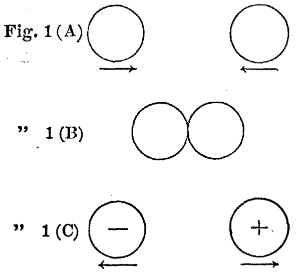


FIG. 1. TRANSMISSION COLLISION BETWEEN TWO ATOMS. IMPROBABLE.

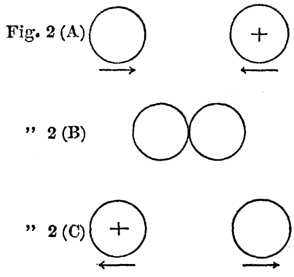


FIG. 2. TRANSMISSION COLLISION BETWEEN AN ATOM AND AN ION. NOT IMPROBABLE.

Three questions will be considered:

1. How numerous must the ions be in order to maintain currents of great density?

2. Would the conductive action of the ions conform to Ohm's law?

3. What should be the temperature relations of conductivity, if it is due to ions?

*1. Requisite Number of Ions per Unit Volume.*—The number of ions required for maintenance of electric currents, even currents of great intensity, may be small compared with the number of atoms—that is, the degree of ionization may be low. To show this let us consider, for example, copper at 300°C. absolute.

German investigators have shown that the specific heats of metals at low temperatures can be satisfactorily accounted for on the hypothesis that the frequency of to and fro vibration of the atoms is nearly independent of the temperature. Grüneisen takes from Nernst and Lindemann 320 as the value of $\beta\nu$ for copper, where $\nu$ is the frequency in question and $\beta = 4.8 \times 10^{-11}$. Accordingly we have

$$\nu = 320 \div 4.8 \times 10^{-11} = 6.7 \times 10^{12}.$$

The distance from center to center of copper atoms at 0° absolute and zero external pressure must be about $2 \times 10^{-8}$ cm., and we may take this as the normal value of the atomic diameter. At ordinary room temperatures the distance from center to center is probably only about 0.5 of 1% greater.

Let us now, taking for simplicity conditions which must be modified later, imagine a row of atoms and ions arranged along a straight line in the direction of the potential gradient, maintained from without, in the metal, the mean distance from center to center being $2 \times 10^{-8}$ cm., and let us suppose each particle to vibrate in its heat motion exactly in the straight line of the row in question, from collision at the left to collision at the right and back again, $6.7 \times 10^{12}$ times per second. Let us suppose every ion in the row to capture an electron at every left-hand collision, thus transferring the ion condition to its left-hand neighbor.

All these assumptions lead to the conclusion that from every ion in the row the ion condition would travel along the row at the rate of $2 \times 10^{-8} \times 13.4 \times 10^{12}$, or 268,000, cm. per second. This is equivalent to one electron traveling with the same velocity. Acting thus one ion per linear centimeter would enable a conductor to maintain a current of $268{,}000 \times 15 \times 10^{-21}$, about $4 \times 10^{-15}$, electromagnetic units; and $10^{15}$ such ions per linear centimeter would carry a current of 40 amperes.

In a copper rod of unit cross-section there are about $88 \times 10^{21}$ atoms per linear centimeter—that is, $3.5 \times 10^{6}$ times the number of ions required to carry a current of 1000 amperes, if these ions were all as effective as they are in this preliminary calculation supposed to be.

We must now let fall some of the favoring assumptions of this calculation, in order to approach more nearly to actual or possible conditions. Instead of assuming every vibration to be in the line of the potential gradient, we must imagine the progress of the ion condition to follow a zig-zag course, the mean distance of travel in the direction of the potential gradient being not $2 \times 10^{-8}$ cm., but, let us say, $10^{-8}$ cm. The great departure, however, from numerical truth was made in assuming that every ion gains an electron at its left-hand collision—that is, at the negative-potential end of its heat path. This is equivalent to assuming that all the existing ions are moving in one direction, from + toward −, through the metal. In fact, the gradient of potential, even if very steep, would probably determine or inhibit the passage of an electron in only a very small proportion of all the collisions between atoms and ions. Let us suppose that a gradient of potential sufficient to maintain a current of 1000 amperes per square centimeter through copper will decide for or against the transition of an electron in one out of every 10,000 atom-ion collisions.

With this revision of our conditions we find that the number of ions required to maintain a current of 1000 amperes per square centimeter is about 1 for every 170 atoms. This degree of ionization, at medium temperatures, does not seem improbable. At least, it cannot be objected to on the ground that it would make the specific heat of the metal too large.

*2. Ohm's Law.*—The mere fact that so small a portion of all the atom-ion collisions need be decisively affected by the potential gradient in order to maintain large currents raises a very strong presumption in favor of the proposition that the number of cases so affected will be proportional to the steepness of this potential gradient. Wherever we find an effect which begins with the beginning of a certain kind of stress and is tested through only a small part of its possible range, the magnitude of the effect in question is found to be proportional to the magnitude of the producing stress.

*3. The Temperature Relation.*—The theory of conduction which we are considering does not, at present, seem capable of giving a satisfactory account of the relation between conductivity and temperature. It would make the conductivity increase, remain constant, or decrease, according to circumstances, with rise of temperature. But, even so, it is worth examining somewhat further; for in some fashion it may at least supplement whatever main theory of conduction shall be found to hold.

In the following discussion certain assumptions are introduced which might require modification upon further study:

A free electron striking an atom is supposed to rebound or to enter the atom driving out another electron.

A free electron striking an ion is supposed always to unite with it to make an atom.

$\Delta$, the total increase of distance from centre to centre of neighboring atoms during the rise of temperature from absolute zero to $T$, is supposed to be proportional to $T$.

$L$, the mean free path of a free electron between collisions, is supposed to be proportional[2] to $\Delta$ and so to $T$.

If $c$ is the mean velocity of the free electrons, the mean time between collisions of an electron is proportional to $T \div c$.

Let $n$ = the number of free electrons, or the number of ions, per unit volume of the metal.

$\tau$, the mean life of an electron in the free state, being terminated only by collision with an ion, is proportional to $(T \div c) \div n$; that is,

$$\tau = q\,T \div n\,c, \tag{1}$$

where $q$ is a constant.

Let $P$ = the number of free electrons produced per unit volume per second. They are supposed to be produced by collisions,—usually by collisions of atoms with atoms, though sometimes by collisions of atoms with ions.

A little consideration shows that

$$P\,\tau = n, \text{ or } P = n \div \tau = n^2\,c \div q\,T. \tag{2}$$

Let $B$ = the total number of *ion* heat-paths begun per unit volume per second.

Let $F$ = the total number of ion heat-paths *finished*, to collision with atom or ion, per unit volume per second.

$F < B$, because of collisions like the one here indicated (fig. 3), in which the ion captures a free electron and ceases to be an ion before it reaches the atom it is approaching.

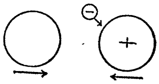


FIG. 3

Let $\theta$ = the mean duration of one heat-path of an atom or an ion. It is inversely proportional to the 'proper frequency' of atomic vibration and may therefore be taken as independent of the temperature.

If an ion could cease to be such only by collision with a free electron, the mean length of life of the ions would be the same as $\tau$, the mean length of life of the free electrons. But an ion may cease to be such by collision with an atom, and the time required for its approach to such a collision is $\theta$. Hence the probability[3] that an ion will survive as such till it has collision with an atom is $\epsilon^{-\theta/\tau}$. Accordingly we have

$$F = B\,\epsilon^{-\theta/\tau} \tag{3}$$

We have now to consider various types of collisions, between atoms, between atoms and ions, or between ions. Some of these may yield free electrons.

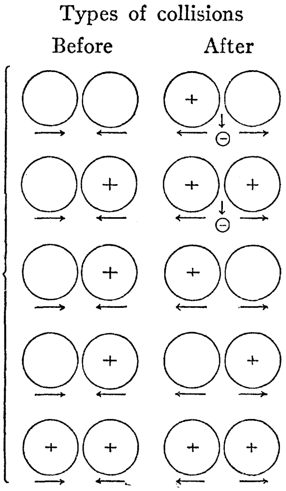
Since all the types of collision in which ions figure are here shown, we have

$$B = P + F \tag{4}$$

From equations (1), (2), (3) and (4) we get

$$F = \frac{n^2c}{qT} \div \left(\epsilon^{(nc\theta \div qT)} - 1\right). \qquad (5)$$

As $F$ is the number of ion heat-paths completed per unit volume per second, we assume that the conductivity is, other things being equal, proportional to $F$. Accordingly our question as to the dependence of conductivity on temperature becomes a question as to the dependence of $F$ on $T$. This in turn, since $n$, $c$ and $T$ are the only variables in the value of $F$, evidently involves the question of the dependence of $c$ and $n$ upon $T$.



| | Contribution to | | |
|---|---|---|---|
| | $B$ | $P$ | $F$ |
| (A) | 1 | 1 | 0 |
| (B) | 2 | 1 | 1 |
| (C) | 1 | 0 | 1 |
| (D) | 1 | 0 | 1 |
| (E) | 2 | 0 | 2 |

7 = 2 + 5

FIG. 4

It is by no means certain that the mean kinetic energy of the free electrons is equal to that of gas molecules at the same temperature. Thus Jeans[4] says, "In this case owing to the small mass of the electron, the frequencies of the vibrations of the medium ['quasi-gas'] constituted by the electrons are very high, so that the old laws of partition of energy will not give anything even approaching a good approximation to the truth." In a paper published in 1914 I reached the conclusion[6] that, in a metal represented by a straight line on the thermo-electric diagram, the mean velocity of the free electrons may be proportional not to $T^{\frac{1}{2}}$, but to $T$, at least approximately.

We shall here use, in turn, the two assumptions:

$$c = \gamma T^{\frac{1}{2}} \quad (6) \qquad \text{and} \qquad c = \gamma T \quad (6'), \qquad \gamma \text{ being a constant.}$$

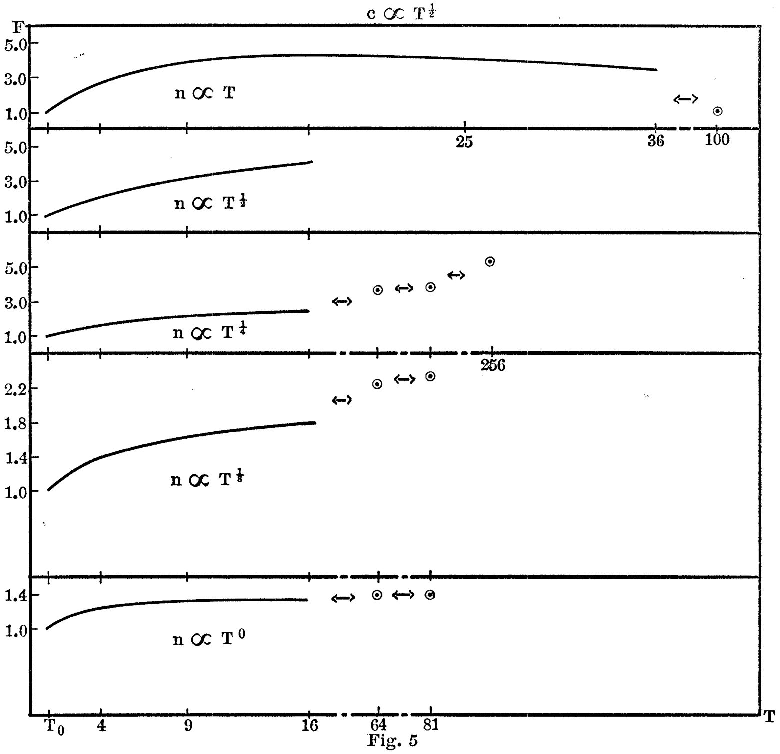

c ∝ T½
F
5.0
3.0
1.0
n ∝ T
25
36
100
n ∝ T½
n ∝ T¼
256
2.2
1.8
1.4
1.0
n ∝ T⅛
n ∝ T⁰
T₀
4
9
16
64
81
T

Fig. 5

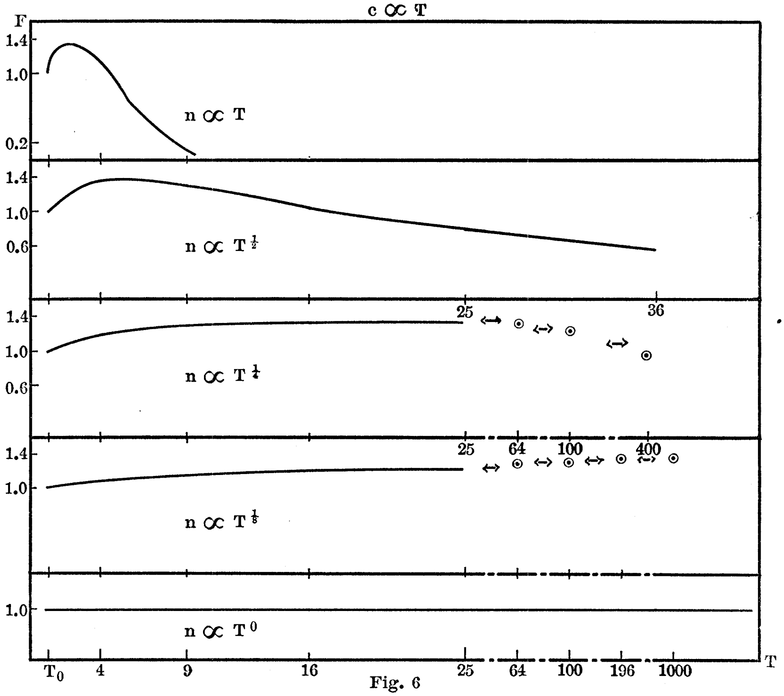

c ∝ T
F
1.4
1.0
0.2
n ∝ T
0.6
n ∝ T½
25
36
n ∝ T¼
25
64
100
400
n ∝ T⅛
n ∝ T⁰
T₀
4
9
16
25
64
100
196
1000
T

Fig. 6

From (5) and (6) we get $F = an^2 \div T^{\frac{1}{2}} (\epsilon^{(bn \div T^{\frac{1}{2}})} - 1)$, (7)

where $a = (\gamma \div q)$ and $b = (\gamma\theta \div q)$, both constant.

We next assume that the relation of $n$ to $T$ is of the form

$n = kT^i$ (8), where $k$ and $i$ are constants.

From (7) and (8) comes $F = ak^2T^{(2i-0.5)} \div (\epsilon^{bkT(i-0.5)} - 1)$. (9)

where $b\ k\ T\ (i - 0.5)$, the exponent of $\epsilon$, is merely another expression for the original $(\theta \div \tau)$.

The lowest temperature to be considered will be called $T_0$, and it will be defined as the temperatures at which $F = \frac{1}{2} B$, which means that only one-half of the ion heat-paths begun are completed by the ions as such.[5]

This makes $\epsilon^{\frac{\theta}{\tau}} = 2$, and so $F = ak^2\, T^{(2i-0.5)}$. Higher temperatures will be expressed as multiples of $T_0$.

Giving to $i$ the values 0, 0.125, 0.25, 0.50, 1.00 and 1.50, in turn, we get from (9) values of $F$ which are indicated by the curves in figure 5.

If, instead of assuming $c \times T^{\frac{1}{2}}$, as in (6) we take $c \propto T$, as in (6′), we get, by making $i = 0$, 0.125, 0.25, 0.50, and 1.00, in turn, values of $F$ which are indicated by the curves, in figure 6.

I have sought to account for the temperature relations of conductivity by combining with the considerations just presented the hypothesis of an atomic vibration consisting of a simple harmonic motion prematurely ended by collision of atom with atom or with an ion. This attempt, though not entirely successful, seemed not altogether hopeless until the experiments of Bridgman showed the atoms to be far less rigid than the kind of vibration in question required them to be.

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[1] It should be, according to Conlomb's law, about $5 \times 10^{-4}$ dyne, corresponding to a potential gradient of about $3 \times 10^3$ volts per centimeter.

[2] This is a doubtful proposition, and possibly some ingenious variation of it would make the ion theory more successful in dealing with the temperature relation.

[3] The question here is analogous to the inquiry what is the probability that a gas molecule will go a distance $x$ without collision, the mean free path being $l$; $\theta$ corresponds to $x$ and $\tau$ to $l$.

[4] Jeans, J. H., *Dynamical Theory of Gases*, 1916, §559.

[5] This does not imply a high degree of ionization. If we assume the electrons to have a mean kinetic energy equal to that of gas molecules at the same temperature, the mean velocity of the electrons will be about 350 times as great as that of the atoms. Hence, if the mean free path of an electron is equal to the mean heat path of an atom or ion, a single electron will have about 350 collisions during the time $\theta$. If $g$ be the degree of ionization,—that is, the ratio of $n$ to the number of atoms per unit volume,—the total number of collisions per second of electrons with ions will be $(350 \div \theta)\ n\ g$. This is the number of ion heat-paths interrupted per second per unit volume by the free electrons. The total number

begun per second is, in the case supposed, $B = P + F = n \div \tau + \frac{1}{2} B$, and so $\frac{1}{2} B = n \div \tau$. Hence $(350 \div \theta)\, n\, g = n \div \tau$, or $g = (\theta \div 350\tau)$. But when $F = \frac{1}{2} B$, $(\theta \div \tau) = \log_e 2$, and so $g = 0.00\,2$ nearly.

[6] Hall, E. H., *Boston, Proc. Amer. Acad. Arts and Sci.*, **50,** 1914, (67–103).

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# THE GRAVIMETRIC SURVEY OF THE UNITED STATES

By William Bowie

DIVISION OF GEODESY, U. S. COAST AND GEODETIC SURVEY

Communicated by W. M. Davis, January 12, 1917

The gravimetric survey of the United States really began in 1890 with the introduction of the Mendenhall one-half second invariable pendulum. Previous to that date, 13 stations had been established but in that older work pendulums were used which gave inaccurate results, as later work showed. We shall not, therefore, consider the gravity results obtained before the use of the Mendenhall pendulum.

This pendulum consists of a bob and stem with a suitable head into which is set an agate plane which rests on a knife edge of the same material fastened to the pendulum case. The various parts of the apparatus are illustrated and described in reports of the Coast and Geodetic Survey.[1] The Mendenhall pendulums are used to determine the difference in the intensity of gravity at two stations.

The probable error of the value of gravity at Washington, determined from Potsdam by the relative method, is ±0.001 dyne. The probable error of a station in the United States, other than that at Washington, is about ±0.002 dyne. This is about one part in one-half million. The error of the absolute value at Potsdam enters all other values of gravity based upon the Potsdam system.

Between the years 1891 and 1907, 47 stations were established in the United States, while since January, 1909, 212 additional stations have been established, making 259 in all. The Coast and Goedetic Survey has planned to continue its gravimetric survey for an indefinite period, with a view to covering the large areas now lacking in stations, and also local areas where there are special problems to be investigated.

There are two immediate purposes to be served in carrying on this work. First, to collect data from which more accurate values may be obtained for the flattening of the earth and for the terms in the gravity formula. Second, to obtain values of the intensity of gravity at laboratories as these values are needed in certain physical and chemical work.

Another important use to which the gravimetric survey may be put is in researches into the subject of isostasy. While an old subject[2] isostasy has only recently become a vital matter to be considered in